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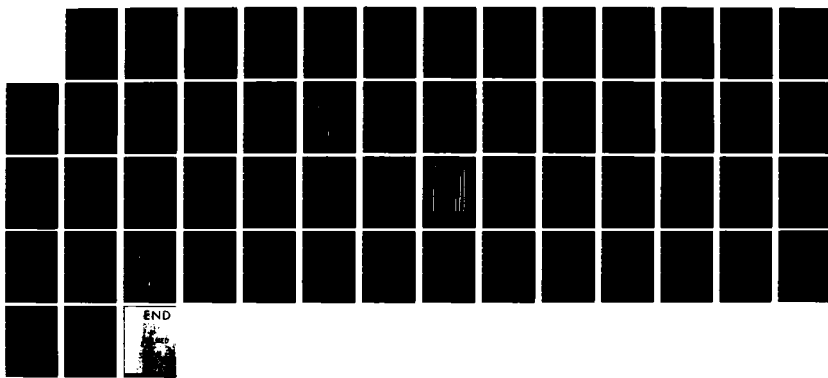
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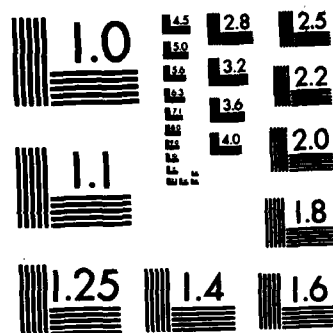
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Progress Report: Oxidation Stability Studies of Deuterated Esters

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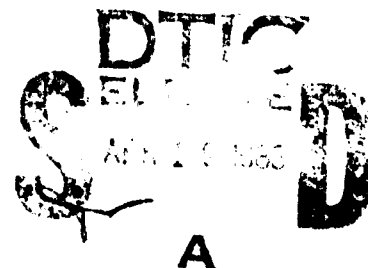
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was obtained at Naval Air Development Center on 97% deuteration of a synthetic hydrocarbon. An additional enhanced lifetime of ~30-fold in the neopentyl polyol esters (deuterated and non-deuterated) appears to be due to an alkali metal effect.

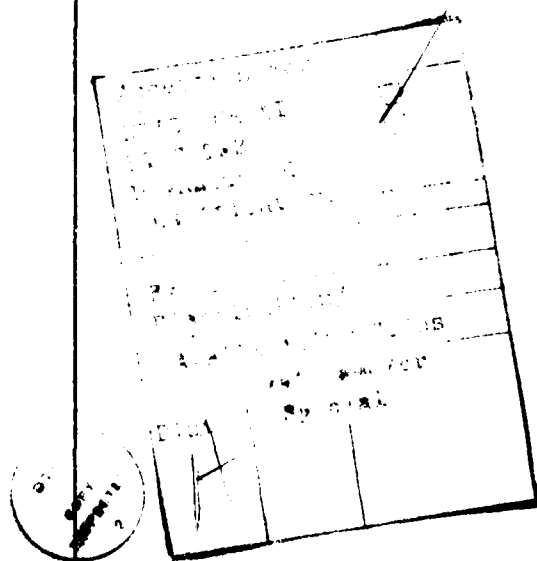


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FOREWORD

This report describes progress on research on the oxidation stability of deuterated esters conducted at the Naval Research Laboratory under contract with Geo-Centers, Inc., Newton Upper Falls, Mass. The responsible NRL investigator is Mr. Harold Ravner.

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EXECUTIVE SUMMARY

In both civilian and military systems the demand for lubricants exhibiting superior performance characteristics over a wide temperature range has increased dramatically since World War II. Neopentyl polyol esters introduced in the 1960s are a group of synthetic lubricants which meet these requirements. These esters exhibit very good thermal and oxidative stability at high temperatures ($>200^{\circ}\text{C}$), excellent viscosity-temperature characteristics, and low pour and freeze points (-55°C). Consequently, for adequate performance at high temperatures ($\sim 220^{\circ}\text{C}$), the neopentyl polyol esters have replaced the petroleum based fluids and the diesters, which were used prior to the 1940s and 1950s, respectively.

A significant increase in lubricant oxidative stability (four fold at 200°C) on 97% deuteration (substitution of hydrogen with deuterium) of a synthetic hydrocarbon formulated as a grease, was first demonstrated by Rebuck and Conte (2) of Naval Air Development Center, Warminster, Pennsylvania. In view of the excellent lubricant properties of the now commonly used neopentyl polyol esters, our research investigated this deuteration effect on the oxidation stability of such an ester. Specifically pentaerythritol tetrahexanoate (PETH) was studied. Preliminary results presented in an earlier Geo-Centers report (1) showed a significant increase in oxidation stability on deuteration of the acid moiety of PETH, i.e., pentaerythritol perdeutero tetrahexanoate (PEdTH). Thus, a fourteenfold increase at 220°C , and a nineteen fold increase at 235°C , indicated the potential of PEdTH as a superior lubricant basestock at high temperatures.

Because of the promising oxidative stability exhibited by PEdTH, the study of deuterated PETH esters was continued. This

study has led to elucidation of certain factors that effect oxidation stability of both non-deuterated and deuterated ester basestocks. Detection of this phenomenon, and identification of the species involved are described following a brief outline of the experimental aspects.

Oxidation tests were generally carried out on the basestocks (2 ml), containing an anti-oxidant (0.5%, octyl PANA: N-p-octyl phenyl-alpha-naphthylamine), with air (flow rate, 20 ml per minute), at 220°C. Oxidation stability of the basestock is measured by its induction period, which is the time elapsed until oxidative degradation occurs. Degradation of the basestock is detected using a gas sensor (1,3). The custom synthesized basestocks were purchased from two commercial laboratories. Hercolube A (Herc A), a commercial lubricant basestock was used as the primary reference. It is a mixed pentaerythritol tetra ester, where the acid moiety is a mixture of C₅- C₉ acids. A sample of PETH from Mobil Oil Company was a second reference.

A wide variation in the oxidation stability was found among different batches of similar basestocks. The variation was independent of the supplier. Average induction periods of three different batches of non-deuterated PETH esters were: 3, 8, and 43 hr. The low induction period (3 hr) was comparable with the reference samples. For similarly deuterated (97%) PEdTH esters, the values were: 9, 105, and 237 hr. The induction period of a totally deuterated ester, perdeutero pentaerythritol perdeutero tetrahexanoate (dPEdTH), was 111 hr. The variability of the results strongly suggested that some unknown species might be responsible for the enhancement of oxidation stability of the non-deuterated as well as the deuterated esters. Consequently, deuteration might not be the sole determining factor in the enhancement of deuterated esters.

The results of a study to identify possible species responsible for the variability in oxidation stability, revealed a correlation between the alkali metal content* of the ester basestock (deuterated and non-deuterated) and its oxidation stability (see Tables S-1 and S-2). Alkali metal compounds thus appear to be the species which enhanced oxidation stability in the pentaerythritol tetra esters screened.** Test of this hypothesis by deliberate addition of sodium carbonate containing 950 ppm sodium to the ester basestocks which had low induction periods (PETH: 3 hr; PEdTH: 9 hr), as well as to dPEdTH (111 hr), and in the presence of an anti-oxidant, confirmed an alkali metal effect. Under similar experimental conditions, the enhanced values were: PETH, 87 hr; PEdTH, 288 hr; dPEdTH, 346 hr.

The alkali metal affect was found to be synergistic with the anti-oxidant; i.e., an anti-oxidant must be present. Occurrence of this synergism is documented in the literature (5, 7). Fig. S-1 shows the effect on oxidation stability of varying concentrations of alkali metal based on the compound added. The basestock employed was a non-deuterated ester which had a low induction period. Consistent with a recent report (7), there is an initial linear increase in induction period with increasing concentration of alkali metal. However, a maximum (100 hr at 220°C) has also been observed, and addition of higher alkali metal concentrations resulted in a decrease of the induction

- * Alkali metal compounds may be incorporated in the basestock during the standard work-up procedure of isolating the tetra ester, since this involves alkali metal salts.
- ** Significantly low levels of sodium (~.02 - 0.13 ppm) were found in the formulated synthetic hydrocarbon and its deuterated analog (see Table S-2). Consequently, the effect of deuteration which was reported (2) to be responsible for the enhanced lifetime of these lubricants appears confirmed.

Table S-1
Spark Emission Spectroscopy Analyses Showing:
Correlation of Induction Period with Sodium Content

Base Stock (CIL) ^a		Elements (1-50 µg/ml) ^b				Induction Period ^c (Hr) at 220°C
		Na	Si	Fe and Ca	B	
PEdTH	F303	+++	+	-	+++	237
PETH	F292	++	+	-	+	41.8
	F304	++	+	-	++	46
	Fraction B					
	#8189 KOR	+	+	-		9.5
	F304	-	+	+	++	3.6
	F146	-	+++	-	-	3.4
	(SiO ₂ treated)					

^a
Unless otherwise specified.

^b
Relative amounts are indicated: +++ ++ +; (-) refers to "not detected". Analysis was carried out at the National Bureau of Standards.

^c
In the presence of octyl PANA (0.5%) as the anti-oxidant.

Table S-2
Flame Emission Spectrometry Analyses¹ Showing:
Correlation of Induction Period with Sodium Content in
Pentaerythritol Tetra Esters²

Base Stock (CIL) ³	Sodium Concentration (ppm)	Induction Period ⁴ (Hr) at 220 ⁰ C
PETH: Herc A ⁵	.02	3.2
Mobil	.15	2.5
F258	.82	2.9
F146 ⁶	1.6	5.7
Fraction A ⁴	2.0	5.3
KOR 8189	5.8	8.4
F304	4.5	3.6
Fraction B	17	46
F292	18	41.8
PEdTH: F145	2.9	9
F303	160	237
KOR 8213 ⁴	3500	106
dPEdTH F144	13	111
Synthetic Hydrocarbon (SHC) ⁷	0.13	3.6 ⁸
Deuterated SHC ⁷	<.02	15.2 ⁸

¹Samples were acid digested and ashed prior to analysis.

²Sodium analysis on deuterated and non-deuterated synthetic hydrocarbons also included to ascertain the enhancement ascribed to deuteration.

³Unless otherwise specified.

⁴In presence of 0.5% octyl PANA.

⁵Mixed pentaerythritol tetra ester (see Appendix A-II).

⁶Non-SiO₂ treated.

⁷Samples supplied by Naval Air Development Center and contain a proprietary formulation.

⁸Oxidation temperature 200⁰C.

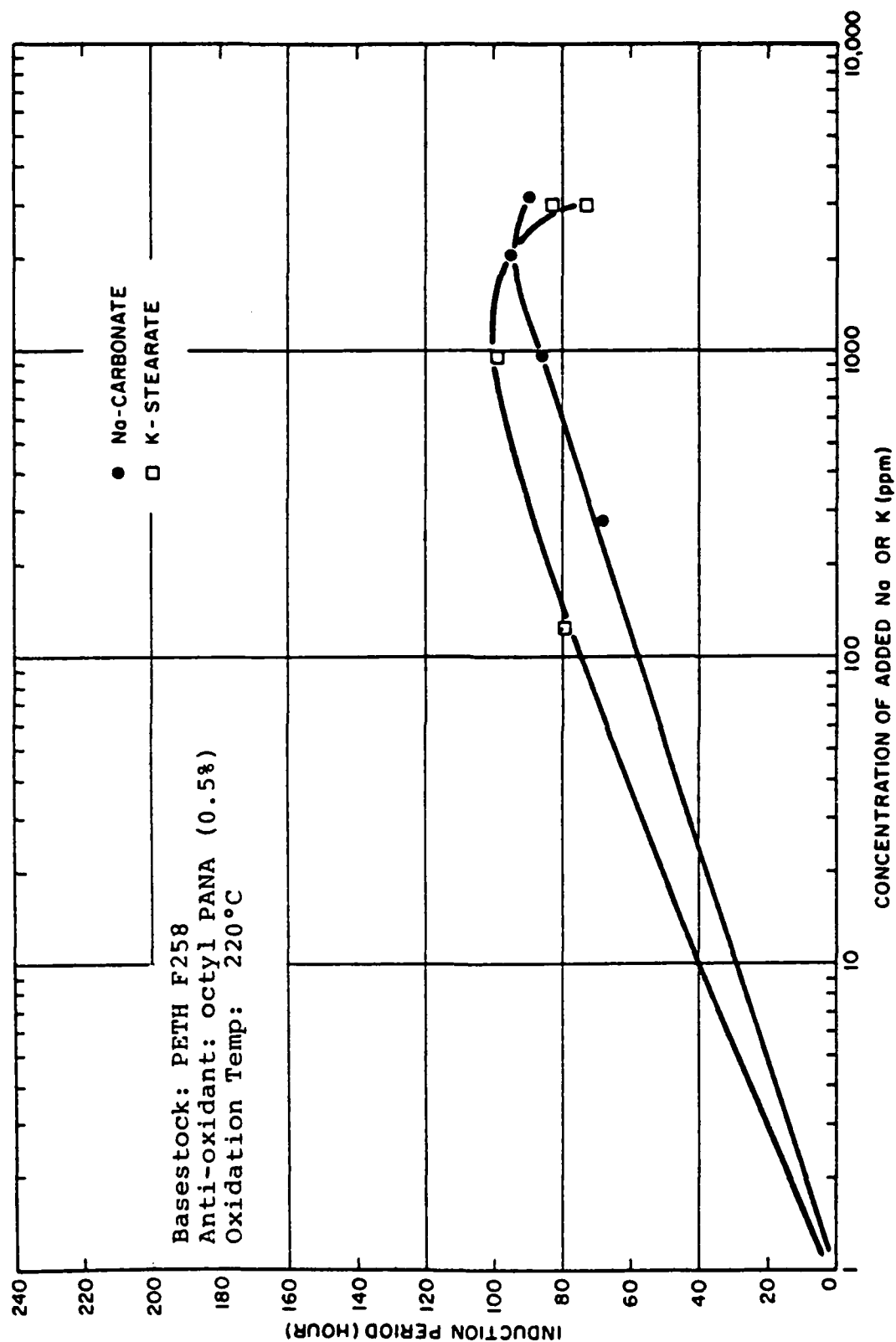


Fig. S-1 - Effect of Added Alkali Metal Concentration on Induction Period

period. In the deuterated esters, a similar alkali metal effect was also observed; viz., an increase and a decrease in induction period with increasing sodium concentration. The maximum induction period obtained (on addition of an alkali metal salt), was 288 hr at 220⁰C in the presence of 0.5% octyl PANA. These results verify that oxidation stability of non-deuterated and deuterated PETH esters is a function of alkali metal concentration. Furthermore, the variation in oxidation stability of the polyol esters (PETH and PEdTH) is explained.

The maximum increase in oxidation stability attributable to an alkali metal effect was found to be approximately thirtyfold in both non-deuterated and deuterated esters. The increase attributable to deuteration was found to be approximately threefold. Since the alkali metal effect is synergistic also with the deuteration effect, the net result is a superior lubricant for high temperature performance. The exceedingly high induction period of a PEdTH ester (237 hr at 220⁰C) which has an inherent sodium content exemplifies this dual effect. Under comparable experimental conditions, the high induction period obtained for a PETH ester with an inherent sodium content was 50 hr. In the absence of sodium, the value for PETH was 3 hr, and for PEdTH, 9 hr.

A successful commercial application of a synthetic lubricant formulated with a soluble sodium compound (perfluoro sodium butanoate) has been reported (7). However, the additional enhancement in oxidation stability (3.6 at 233⁰C, in the presence of an anti-oxidant) due to deuteration, has been confirmed in the comparative evaluation between a PEdTH ester, which has an inherent sodium content, and Herc A, to which sodium acetyl acetate was added.

Preliminary oxidation-corrosion tests similar to that described in the Military Specification publication

(MIL-L-23699A) were performed in the presence of steel, titanium, silver, and aluminum at 220⁰C. The effect of an anti-wear additive, tricresyl phosphate (TCP, 1%), was also investigated in these tests and found to have an adverse effect on oxidation stability. The results were compared with the performance of Herc A under similar experimental conditions and are shown in Fig. S-2. Despite the effect of TCP, both deuteration and the presence of alkali salts again significantly enhanced oxidation stability.

These results confirm a PEdTH ester to be a superior lubricant basestock for high temperature performance (220⁰C - 235⁰C). Consequently, further testing is warranted for its qualification relating to a specific application. (See Recommendations).

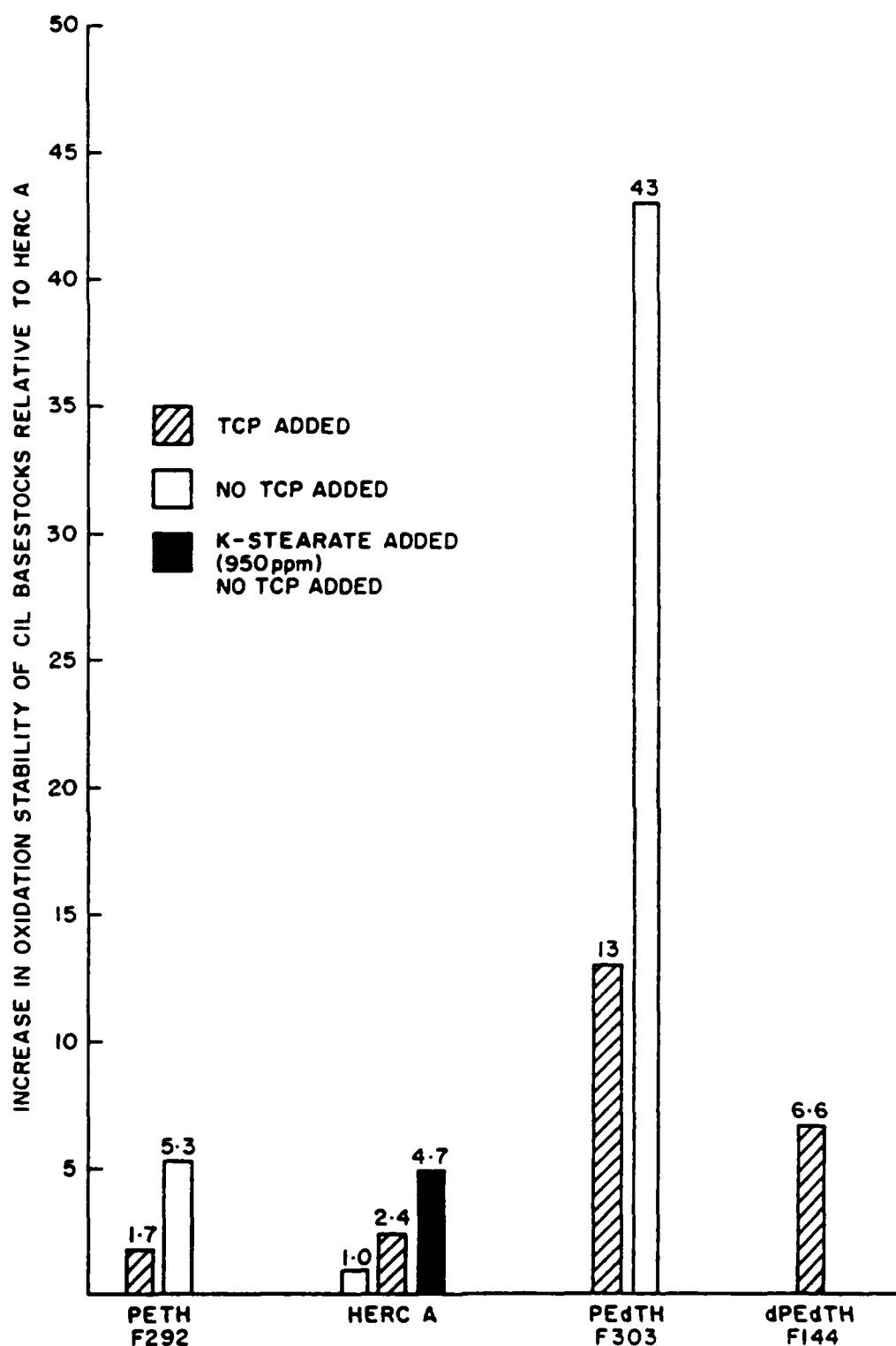


Fig. S-2 - OXIDATION-CORROSION TESTS - Comparison of Deuterated and Non-deuterated Basestocks, with Herc A, in presence of: Ag + Al + Ti + Fe, with and without TCP (1%). Anti-oxidant: 0.5% octyl PANA; Oxidation Temp: 220°C

1. INTRODUCTION

In an earlier report (1) on the oxidation stability of deuterated lubricants, preliminary results indicated pentaerythritol perdeuterotetrahexanoate to be promising as a superior lubricant basestock especially for high temperature performance (220-235⁰C). Consequently, replacement of the formulated non-deuterated pentaerythritol tetra esters currently used with the formulated deuterated analogs, can have significant applications both in military and civilian systems. For example, guidance systems, satellites, and in maintenance operations where labor costs are high, the deuterated lubricants become cost-effective. (1)

Pentaerythritol tetraesters have commercial and military applications as lubricant basestocks because of their excellent physical and chemical properties over a wide temperature range (-55 to 260⁰C). Moreover, on degradation, the oxidation products are not as susceptible to sludge formation as hydrocarbon or petroleum oils.

An increase in lubricant oxidative stability on deuteration was first reported by Rebuck and Conte (2): At 97% level of deuteration of a synthetic hydrocarbon formulated as a grease, a fourfold increase in oxidation stability was obtained at 200⁰C. Deuteration of esters, likewise resulted in an increase in oxidation stability. Specifically (1), an increase in oxidation stability of fourteen-fold at 220⁰C, and nineteen-fold at 235⁰C, was obtained with pentaerythritol perdeutero tetrahexanoate (deuteration of the acid moiety of the ester).

In this report, the continuing study of deuterated and non-deuterated pentaerythritol tetrahexanoate esters was divided into 4 areas:

In Section 2, a comparative evaluation of the oxidation stabilities of deuterated and non-deuterated pentaerythritol tetrahexanoate basestocks from a second supplier is discussed.

In Section 3, characterization of the basestocks is described. This study led to an elucidation of certain factors that effected oxidation stability of both non-deuterated and deuterated ester basestocks.

In Section 4, the oxidation stabilities of the basestocks are evaluated with a commercial lubricant, employing two different anti-oxidant formulations.

Finally, in Section 5, the results of some preliminary oxidation-corrosion tests on the basestocks are given.

A description of the "'Experimental'" is given in the Appendix.

2. EVALUATION OF OXIDATION STABILITIES OF DEUTERATED AND NON-DEUTERATED PETH BASESTOCKS

2.1 RESULTS AND DISCUSSION

The induction periods of the basestocks screened are shown in Table I. The results (illustrated in Fig. 1) indicate a wide variation in oxidation stability of similar basestocks from different batches; moreover, this variation was independent of the supplier. The variation found among similarly deuterated (~97%), PEdTH esters, as well as the non-deuterated PETH esters, is discussed below.

The earlier work (1,3) on the effect of deuteration on oxidation stability of an ester was carried out on PETH, and PEdTH purchased from KOR. Consequently, in an evaluation of similar esters from CIL, the KOR esters were used as a reference.

Among the CIL PETH esters, the induction period varied from 3-46 hrs. The low induction period (~3 hr) obtained in certain batches was comparable with that of Herc A and the sample from Mobil, but was about one third that of the sample from KOR. Other samples from CIL, namely, F292 and Fraction B ex F304, had an approximate five-fold increase in oxidation stability compared with KOR PETH. This result inferred that the relative increase of the deuterated KOR PEdTH was now only about 2.4 times that of a non-deuterated PETH ester. Consequently, an enhancement of fourteen-fold which was reported (1,3) as an effect of deuteration has been re-examined as part of the study.

Among the CIL PEdTH esters, the 2 batches (F145, F303) evaluated were as similarly deuterated as the KOR PEdTH (97%). The wide variation in oxidation stability (9-237 hr) of the batches (see Fig. 1) suggested that factors other than deuteration

Table I. Variation in Induction Period of Non-deuterated PETH, and Deuterated (97%) PE_dTH, dPE_dTH Basestocks from Different Suppliers. Basestocks contained 0.5% octyl PANA. Oxidation temperature was 220°C.

Supplier	Induction Period Hr.		Relative Increase ¹	
	Deut. Ester	Non-Deut. Ester		
KOR	PE _d TH: # 8213	PETH: #8189	102.4 7.3	14 ² 11.5
			109 9.5	
Hercules Powder Co.		Herc A ³	3.2	
Mobil		MCP 386	2.5	
		Perc ⁴	2.6	
CIL	F145 SiO ₂ 9 treated	F146 SiO ₂ treated	3.4	2.4
	Perc ⁴ "	F146 Non "	5.7	
		F258	2.9	
		F292	41.8	
	F303	F304	3.6	
		" Fr. A	5.3	
		" Fr. B	46	~ 5
	dPE _d TH F144		111	

¹ Ratio of induction periods: Deuterated/Non-Deuterated.

² Previous data reported. See Ref. 1.

³ Mixed pentaerythritol tetra ester (see Appendix A-II).

⁴ Percolated through basic alumina and Florisil.

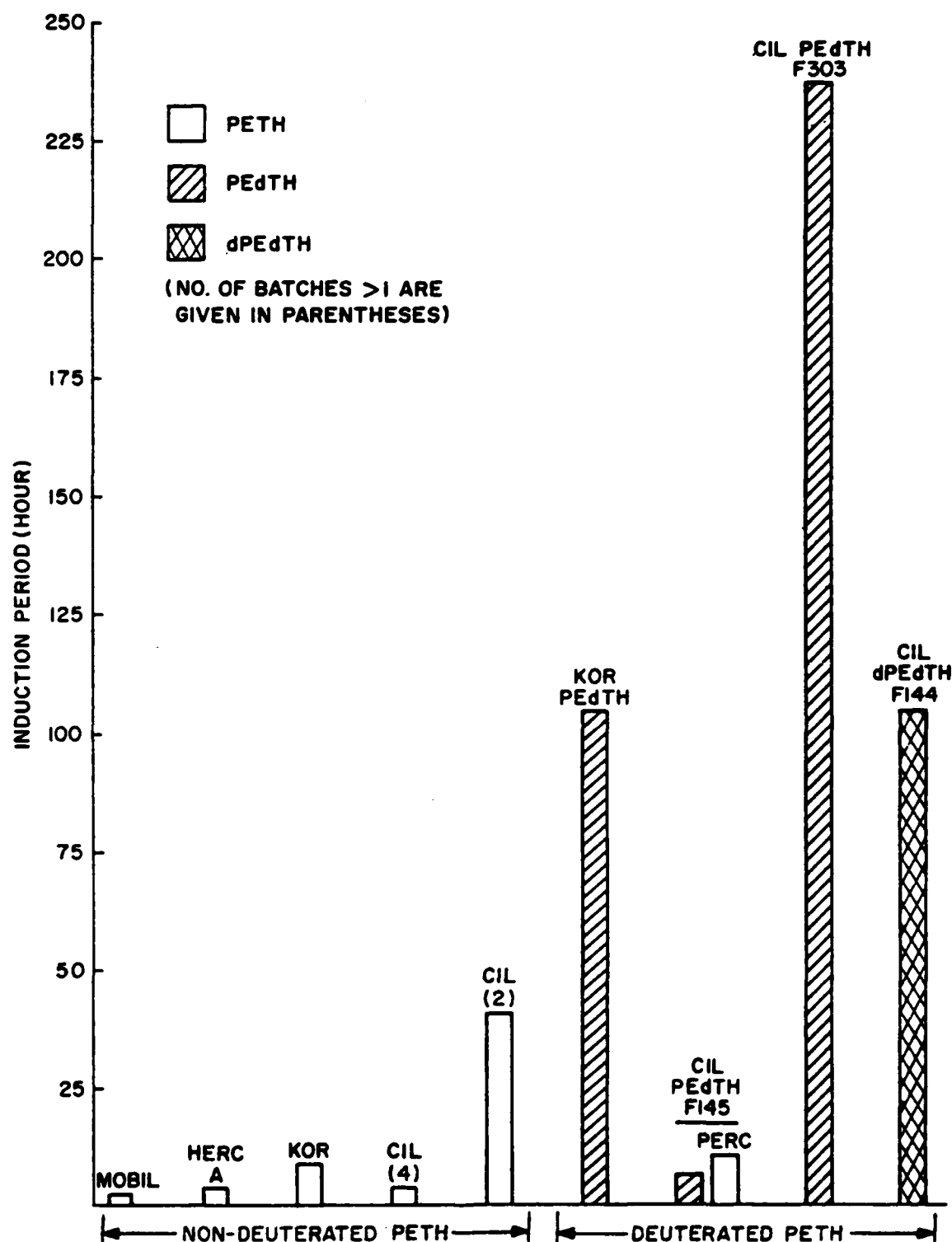


Fig. 1 - Variation in Induction Period Among Different Batches of Similar Basestocks Supplier Independent. Anti-oxidant: 0.5% octyl PANA; Oxidation Temp: 220°C

might be responsible. The exceedingly low induction period of PEDTH F145 (9 hr), which is comparable with that of a non-deuterated PETH (KOR), confirmed this view. Percolation of the F145 through basic alumina to remove acidic impurities, did not significantly improve its oxidation stability (12 hr), in spite of the removal of tri-esters (see Table II). The induction period of F303 was twice that of KOR PEDTH. The very high induction period of PEDTH F303, (237 hrs with 0.5% octyl PANA, at 220⁰C oxidation temperature), is important in itself for it offers tremendous potential as a superior lubricant basestock at high temperatures (220-235⁰C). The induction period of a totally deuterated ester dPEDTH CIL F144 was found to be about one-half that of a partially deuterated PEDTH ester (F303), but similar to KOR PEDTH.

2.2 CONCLUSION

The variability of the results described strongly suggests that deuteration may not be the sole determining factor in the enhancement of oxidation stability of deuterated esters. Furthermore, there appears to be some unknown species that enhanced the oxidation stability of both the non-deuterated and deuterated basestocks screened. This aspect is investigated in the characterization of the deuterated and non-deuterated PETH esters. An underlying objective on identification of the species effecting oxidation stability, would be to obtain basestocks with reproducible oxidation stability.

3. CHARACTERIZATION OF THE DEUTERATED AND NON-DEUTERATED ESTERS

A plausible explanation of the previously mentioned variation in oxidation stability of similar basestocks was the degree of purity of the sample. Sample purity is dependent on the extent of esterification (preparative aspect), as well as on the techniques in isolation of the tetra ester (work-up procedure). An outline of the preparation and a general protocol for isolation of PETH ester is given in Appendix A.

The purity of the basestocks was investigated using various analytical methods: GC-Mass Spectrometry, High Performance Liquid Chromatography (HPLC), Nuclear Magnetic Resonance Spectroscopy (NMR), Fourier Transform Infrared Spectroscopy (FTIR), and Thermogravimetric Analysis (TGA). Results of the analyses indicated differences among similar basestocks. Differences in tri-ester concentration among similar basestocks were observed particularly in the NMR and FTIR analyses. Capillary GC-Mass Spectrometry also would be very useful in future analyses of the basestocks.

Identification of the species involved in the enhancement of oxidation stability led to the following investigations: the roles of tri-esters and alkali metal compounds. Alkali metal compound(s) may be incorporated in the basestock during the work-up procedure.

3.1 ROLE OF TRI-ESTERS: (SEE TABLE II)

Incomplete esterification will result in the presence of tri-esters. Even at a 95% level of esterification there is a high level (~20%) of tri-esters with the remaining ~80% being tetra

Table II. Nor-Correlation of Induction Period
with Tri-Ester Content

Base Stock (CIL) ^a	Tri-Ester ^b (%)	Induction Period ^c (Hr)
PETH: F258	<<5	2.9
#8189 KOR	<<5	9.5
F304	5	3.6
F304 Fr. A	5	4.5
F304 Fr. B	5	46
F146 ^d	10	3.4
F292	10	41.8
PEdTH: #8213 KOR	<<5	109
F145	10	9
Perc ^e F145	<<5	12
F303	20	237
dPEdTH F144	10	111

^a Unless otherwise specified.

^b Determined via FTIR analyses.

^c In the presence of octyl PANA (0.5%) as the anti-oxidant.

^d Silica treated.

^e Percolated through a column of basic alumina.

ester. FTIR analyses of the various basestocks indicated the presence of tri-esters (~5-20%).

As shown in Table II there is a wide variation in oxidation stability of similar basestocks containing similar levels of tri-ester. In the case of the PEdTH esters, the low induction periods obtained with CIL F145 (9 and 12 hr), cannot be explained on the basis of its tri-ester content (10% and <<5%, respectively), since high induction periods have been obtained with other PEdTH basestocks containing similar low concentration of tri-esters (KOR 109 hr; <<5% tri-ester), as well as higher concentration of tri-esters (CIL F303 237 hr; 20% tri-ester). In conclusion, the role of tri-esters at the levels studied does not appear significant.

3.2 ROLE OF ALKALI METAL

3.2.1 INTRODUCTION

Alkali metal salts are used in the standard work-up procedure involving the isolation of esters (see Appendix A, "Isolation of PETH"). The incorporation of alkali metal compounds in the basestock during the work-up procedure may depend on their origin (e.g., sodium salts of tri-esters, or carbonates, etc), and the extent of treatment (e.g. reprocessing). The importance of the method used in reprocessing was reflected in the significant enhancement in oxidation stability of a certain basestock. Thus, as shown in Table I, Fraction B (see Appendix A-IIB for a description of the basestocks) showed a ninefold enhancement versus Fraction A.

The effect of metals and metal compounds especially the alkali metal compounds in extending the oxidation stability of the lubricant is well documented in the literature (4-7). Consequently, the fortuitous incorporation of alkali metal compounds in varying amounts may well explain the variability in oxidation stability of similar basestocks. This hypothesis was tested in

a follow-up investigation of the effect of alkali metal concentration on the oxidation stability of the basestocks screened.

3.2.2 INVESTIGATION: EFFECT OF ALKALI METAL CONCENTRATION ON OXIDATION STABILITY OF DEUTERATED AND NON-DEUTERATED PETH ESTERS

This investigation was performed by the following 2 methods. A differentiation of the alkali metal effect from the deuteration effect was investigated concomitantly:

3.2.2A Metal-analysis of Deuterated and Non-deuterated Basestocks:

A preliminary analysis using Spark Emission Spectroscopy revealed the presence of varying amounts (1-50 ppm) of sodium as well as silicon, iron, calcium, and boron (see Table III-A). Levels less than 1 ppm were not detected. Although the data was semiquantitative, it showed nevertheless, a definitive correlation of induction period with sodium content: Basestocks in which no sodium was detected, but contained an anti-oxidant exhibited low induction periods (~3-4 hr); also, the induction period increased with increasing sodium content.

Data obtained from the analysis for sodium, using Flame Emission Spectrometry (see Table III-B), verified the correlation of an increase in the induction period with increasing sodium content in the esters screened. This correlation was found in both non-deuterated and deuterated PETH basestocks. However, the PEdTH basestocks, which contained high concentrations of sodium (160-3500 ppm), further exhibited (see Fig. 2A) a maximum in the induction period at ~200 ppm sodium. The presence of higher concentrations of sodium (>200 ppm) resulted in a decrease in induction period.

Table III-A
Spark Emission Spectroscopy Analyses Showing:
Correlation of Induction Period with Sodium Content

Base Stock (CIL) ^a	Elements (1-50 µg/ml) ^b				Induction Period ^c (Hr) at 220°C
	Na	Si	Fe and Ca	B	
PEdTH F303	+++	+	-	+++	237
PETH F292	++	+	-	+	41.8
F304	++	+	-	++	46
Fraction B					
#8189 KOR	+	+	-		9.5
F304	-	+	+	++	3.6
F146 (SiO ₂ treated)	-	+++	-	-	3.4

^a
Unless otherwise specified.

^b
Relative amounts are indicated: +++ ++ +; (-) refers to "not detected". Analysis was carried out at the National Bureau of Standards.

^c
In the presence of octyl PANA (0.5%) as the anti-oxidant.

Table III-B
Flame Emission Spectrometry Analyses¹ Showing:
Correlation of Induction Period with Sodium Content in
Pentaerythritol Tetra Esters²

Base Stock (CIL) ³	Sodium Concentration (ppm)	Induction Period ⁴ (Hr) at 220 ⁰ C
PETH: Herc A ⁵	.02	3.2
Mobil	.15	2.5
F258	.82	2.9
F146 ⁶	1.6	5.7
Fraction A ⁴	2.0	5.3
KOR 8189	5.8	8.4
F304	4.5	3.6
Fraction B	17	46
F292	18	41.8
PEdTH: F145	2.9	9
F303	160	237
KOR 8213 ⁴	3500	106
dPEdTH: F144	13	111
Synthetic Hydrocarbon (SHC) ⁷	0.13	3.6 ⁸
Deuterated SHC ⁷	<.02	15.2 ⁸

¹Samples were acid digested and ashed prior to analysis.

²Sodium analysis on deuterated and non-deuterated synthetic hydrocarbons also included to ascertain the enhancement ascribed to deuteration.

³Unless otherwise specified.

⁴In presence of 0.5% octyl PANA.

⁵Mixed pentaerythritol tetra ester (see Appendix A-II).

⁶Non-SiO₂ treated.

⁷Samples supplied by Naval Air Development Center and contain a proprietary formulation.

⁸Oxidation temperature 200⁰C.

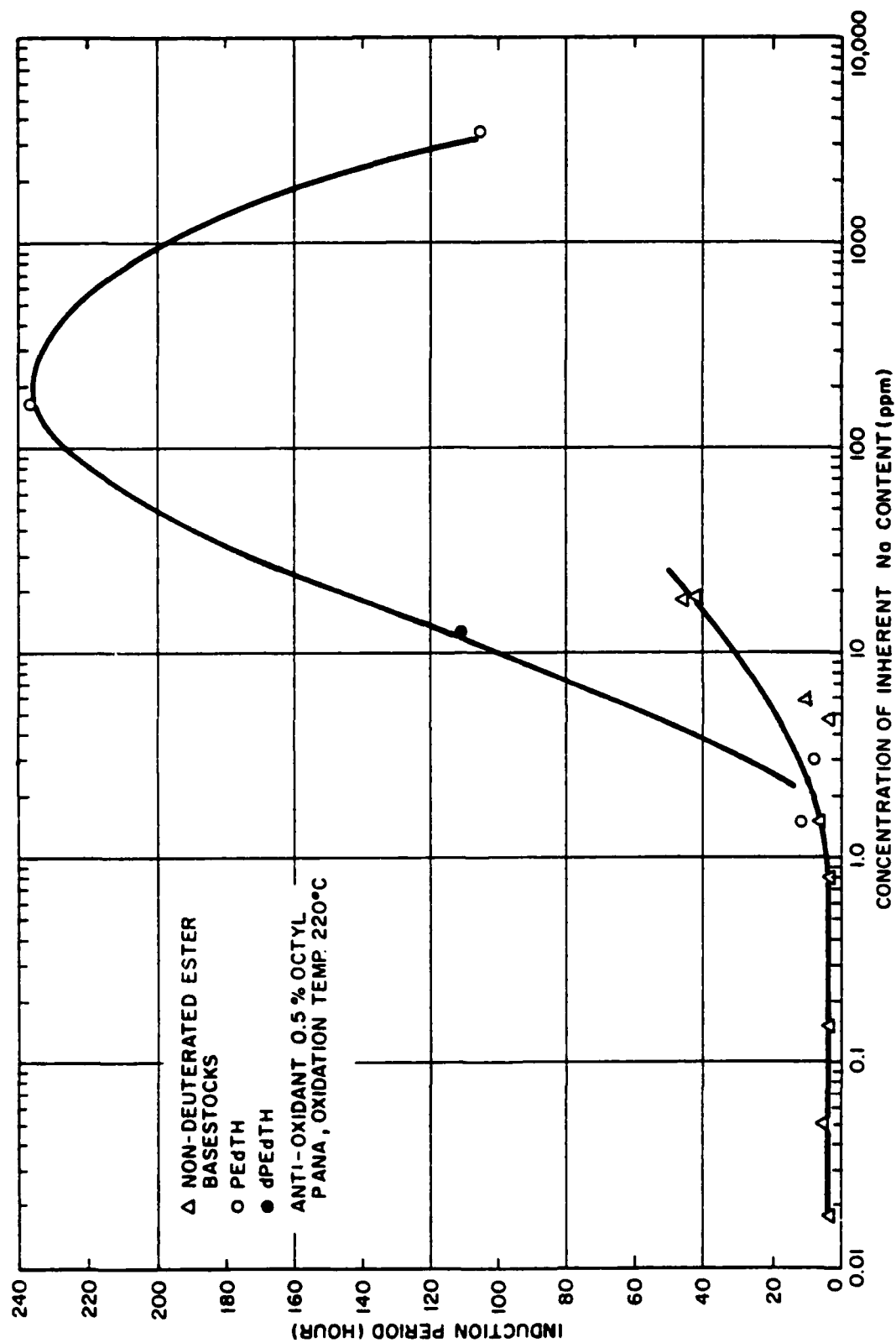


Fig. 2A - Effect of Inherent Sodium Concentration on Induction Period of Basestocks Screened

Since the results are based on the inherent sodium content of these basestocks, the data are limited to the samples received. Consequently, in certain cases, the results shown in Fig. 2A indicate trends rather than absolute values. For example, the maximum in the induction period of the deuterated esters should not be considered an absolute value. In spite of the limited data, an enhancement in oxidation stability attributable to deuteration is suggested (cf. oxidation stabilities of deuterated vs. non-deuterated basestocks at ~5-20 ppm inherent sodium content as shown in Fig. 2A). Furthermore, no enhancement in oxidation stability due to an alkali metal effect was observed below a sodium concentration of approximately 1 ppm.

In the case of the synthetic hydrocarbons, which were included in this analysis (see Table III-B), only very low levels of sodium were found in both non-deuterated (0.13 ppm), and deuterated (<.02 ppm) formulated basestocks. Consequently, these results seem to confirm the enhancement in oxidation stability (fourfold at 200°C) of the deuterated analog to be attributable to a deuteration effect (2).

3.2.2B Addition of Varying Amounts of Sodium or Potassium Compounds:

Alkali metal compounds containing ~100-3000 ppm alkali metal were added to the basestocks containing the usual concentration of anti-oxidant (0.5% octyl PANA). Both non-deuterated PETH, and deuterated (PEdTH and dPEdTH) esters with varying sodium content were thus screened. However, basestocks with low sodium content (<5 ppm) were employed in a controlled study of the effect of alkali metal concentration on induction period. The results are illustrated in Figs. 2B and 3.

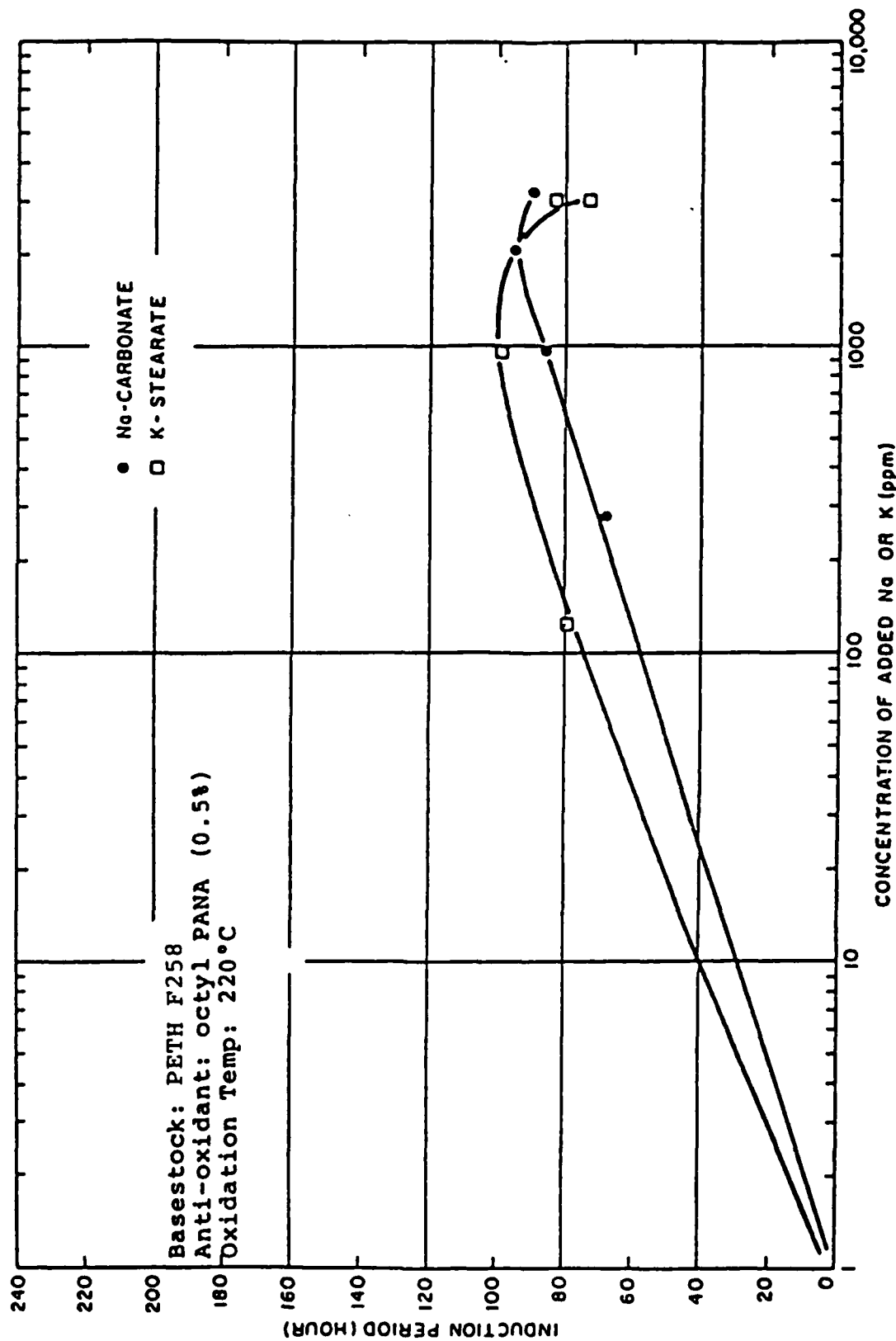


Fig. 2B - Effect of Added Alkali Metal Concentration on Induction Period

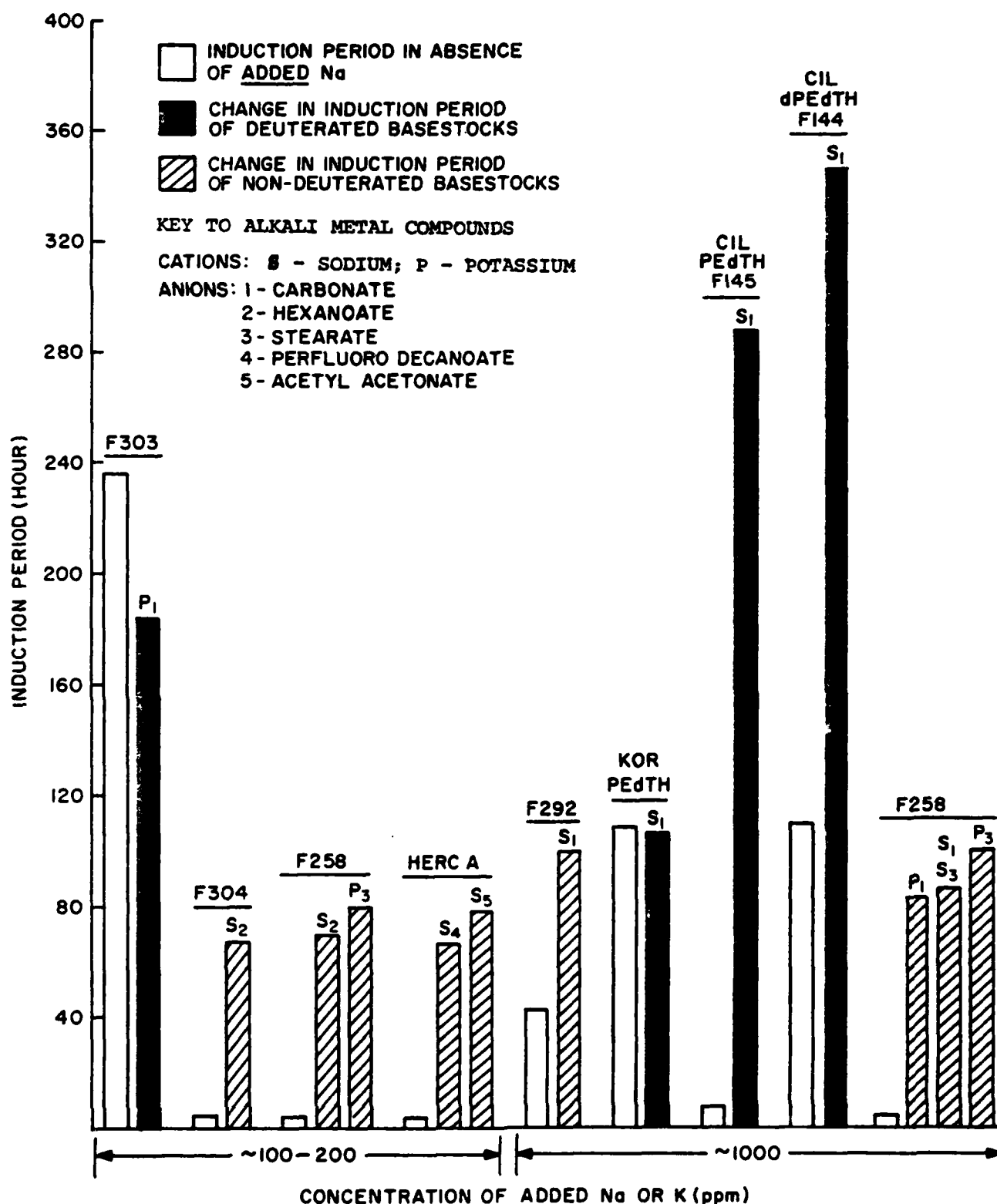


Fig. 3 - Relative Change in Induction Period on Addition of Na/K Compounds (100-1000 ppm): Non-deuterated and Deuterated Basestocks Screened in presence of 0.5% octyl PANA at 220°C

A linear increase in induction period with increasing concentration of alkali metal (0-180 ppm) has been reported by Chao and Kjonaas (7). As shown in Fig. 2B, initially, the induction period of a PETH ester containing ~1 ppm sodium was also found to increase linearly with increasing concentration of sodium or potassium. However, a maximum in the induction period was observed, similar to that found in the PEdTH esters with inherently high sodium content (160-3500 ppm). Addition of higher concentrations of alkali metal likewise resulted in a decrease of the induction period. This oxidation stability triad sequence: increase - maximum - decrease, resulting from increasing alkali metal concentration, will be referred to as an alkali metal effect.

A similar controlled study of the alkali metal effect in PEdTH esters containing low levels of sodium was somewhat limited for sample availability reasons. Nevertheless, the data obtained (see Fig. 3) corroborated previous observations (see also 3.2.2A) of an "alkali metal effect" being operative in both non-deuterated and deuterated basestocks. In addition to the oxidation stability triad sequence mentioned earlier, a subsequent leveling effect is inferred on further increase in alkali metal concentration. Thus, KOR PEdTH which has a low induction period (102-109 hr, sodium content 3500 ppm), compared with PEdTH F303 (237 hr., sodium content 160 ppm), exhibited no further change in oxidation stability on addition of sodium carbonate (950 ppm sodium).

Since the "alkali metal effect" appears to be concentration dependent, its role in the enhancement of oxidation stability should be significant in samples with inherently low sodium content. The data illustrated in Fig. 3 verified this hypothesis. Thus, both non-deuterated (Herc A, PETH: F258, F304) and deuterated (PEdTH F145) basestocks, which had inherently low levels of sodium (~.02-5 ppm, see Table II-B), exhibited 20-30 fold enhancement on addition of sodium or potassium compounds

(~100-1000 ppm alkali metal). A comparison with other basestocks (dPEdTH F144, PETH F292) which had inherently higher levels of sodium (~13-18 ppm) exhibited only 3-4 fold enhancement.

In a subsequent investigation of the role of alkali metal compounds, their reported synergistic effect with the antioxidant, (5, 7) was also observed. Thus, the induction period of a basestock and added sodium salt (Na_2CO_3 , 950 ppm), with no anti-oxidant present was extremely low (0.16 hr.). In the presence of an anti-oxidant, however, and comparable concentration of sodium carbonate the value was 87 hr., under similar oxidation conditions. With the omission of sodium carbonate, but with an anti-oxidant present, under comparable conditions, the value was 3 hr.

3.2.3 DIFFERENTIATION OF THE SYNERGISTIC EFFECT OF ALKALI METAL COMPOUNDS FROM THE DEUTERATION EFFECT

These oxidation tests were performed under the usual oxidation conditions, i.e., at 220°C , and in the presence of 0.5% octyl PANA as the anti-oxidant. Consequently, the enhancement factors obtained refer specifically to these conditions.

The maximum induction periods obtained for PETH, PEdTH, and dPEdTH in the presence of similar amounts of added sodium carbonate (950 ppm, sodium) were 87 hr., 288 hr., and 346 hr., respectively. The induction periods obtained for PETH and PEdTH containing inherently low and non-effective concentrations of sodium (<5 ppm) were 3 hr., and 9 hr., respectively. Consequently, as shown in Table IV, the enhancement in oxidation stability attributable to a 97% deuteration effect is approximately threefold. The maximum enhancement attributable to an alkali metal effect is approximately thirtyfold. The maximum net increase in oxidation stability of 97% deuterated esters thus appears to be a product of these two effects (see Table IV).

Table IV. Differentiation of the Synergistic Alkali Metal Effect from the Deuteration Effect

Basestock	Induction Period ^a (Hr) at 220°C Varying			Enhancement due to:		
	Alkali Metal Effectiveness (AME)	Intermediate ^c	Maximum ^d	Deuteration ^e	AME ^f	Combined Effect ^g
	None ^b					
PETH F258	3		87		29	
PEdTH F145	9		288	3 ^b , 3.3 ^d	32	96
dPEdTH F144		111	346	4 ^d		

^a 0.5% octyl PANA present.

^b Inherent sodium content: 1 ppm found non-effective (see Fig. 2A).

^c Inherent sodium content: 13 ppm (see Fig. 2A).

^d Added sodium carbonate (950 ppm sodium).

^e Ratio of induction period: Deuterated/Non-deuterated at similar alkali metal concentration.

^f Ratio of induction period of similar basestocks: Maximum AME/None.

^g Product of Deuteration Effect and AME

3.2.4 CONCLUSION

The results on oxidation stability of pentaerythritol tetra ester basestocks in which alkali metal compounds are present inherently (incorporated in the work-up procedure), are in agreement with the data obtained in which this effect is simulated by deliberate addition of alkali metal compounds to the basestocks. Consequently, the alkali metal content of the ester basestocks screened seems to determine the oxidation stability of both non-deuterated and deuterated pentaerythritol tetrahexanoate esters. The additional enhancement in oxidation stability of deuterated esters when similarly compared with non-deuterated esters (in presence of similar alkali metal concentrations) confirms a deuteration effect. Enhancement (fourfold at 200⁰C) in oxidation stability of the deuterated synthetic hydrocarbon, attributed (2) to a deuteration effect was also confirmed.

The significant enhancement in oxidation stability that is observed in deuterated esters in the presence of an anti-oxidant, appears to be the product of two effects, viz, the alkali metal effect (the major contributing factor) times the deuteration effect. The effect of total deuteration versus partial deuteration under similar conditions resulted in only a small increase (~20%) in oxidation stability at 220⁰C. This observation suggests that for commercial applications, no significant advantage may be gained by using a totally deuterated ester (dPEdTH). Further study of dPEdTH is necessary to confirm our results.

4. EVALUATION OF PEDTH AND PETH ESTERS WITH A COMMERCIAL LUBRICANT (HERC A) EMPLOYING 2 DIFFERENT ANTI-OXIDANT FORMULATIONS

4.1 ANTI-OXIDANT SYSTEM: 1% W/W PANA (PHENYL-ALPHA NAPHTHYLAMINE) + 0.1% W/W ALKALI METAL COMPOUND

Although the synergistic alkali metal effect is tremendous (~ thirty-fold relative increase in oxidation stability at 220⁰C), practical application of alkali metal compounds is limited by their solubility. However, in a recent publication by Chao (7) and Kjonaas, the authors reported a successful commercial application on a synthetic lubricant containing an alkali metal compound as a synergistic anti-oxidant; the aircraft engines tested were eight JT8D, and a patent has been issued (U.S. Patent 3,329,611) on the system used: a formulated Type II synthetic lubricant containing 0.06% perfluoro sodium butanoate.

In view of the cost factor involved in deuteration, it was therefore important to comparatively evaluate PEDTH F303, with a similar system reported by Chao and Kjonaas. This system involved Herc A containing 1% PANA + 0.1% (w/w) alkali metal compound at an oxidation temperature of 233⁰C (450⁰F). The alkali metal compounds which were reported (7) to be most effective were: sodium acetylacetonate (Na Acac) and perfluoro sodium butanoate (C₃F₇COONa). Result of such an evaluation using Na Acac, which was also found to be comparable with C₃F₇COONa (7), is shown in Table V. A relative increase in oxidation stability of 3.6 fold was found in PEDTH F303, compared with Herc A + Na Acac. As is shown in Fig. 3, the efficacy of Na Acac or C₉F₁₉COONa (perfluoro sodium decanoate was used instead of the butanoate for availability reasons) in Herc A, is comparable with other sodium compounds screened using PETH esters.

Table V. Evaluation of PETH and PEDTH Basestocks with Herc A and Certain Anti-oxidants Used Commercially, at Different Temperatures

Anti-Oxidant Formulation	Base Stock	Anti-Oxidant (% w/w)	Added Na (ppm)	Temp (°C)	Induction Period (Hr)	Increase Rel. to Herc A
Chao ⁷	Herc A	PANA, 1%	None	233	2	
	Herc A	PANA, 1%	Na Acac 185 ^b	233	36.9	
	F303	PANA, 1%	None ^c	233	132	3.6
	F292	PANA, 1%	None ^c	233	16.2	
Commercial	Herc A	PANA, 1% + DODPA, 1%	None	220	27	
	F292	PANA, 1% + DODPA, 1%	None ^c	220	109.9	4

^a Herc A is a commercial lubricant, and is used as a Reference.

^b Equivalent to 0.1% w/w, concn. used by Chao (7).

^c Sodium salts present inherently.

In conclusion, PE_dTH is a superior lubricant basestock compared with a non-deuterated ester containing a relatively soluble sodium compound. The relative enhancement in oxidation stability of PE_dTH is similar to the results obtained previously for a deuteration effect (see Conclusion, Section II).

4.2 COMMERCIAL ANTI-OXIDANT FORMULATION: 1% W/W PANA (P-ALPHA-NAPHTHYLAMINE) + 1% W/W DODPA (DI-OCTYL-DIPHENYLAMINE)

These results are included in Table V. Only a non-deuterated ester PETH F292 was screened because its induction period was so high (109 hr, at 220⁰C). Since the induction period decreases with increase in oxidation temperature, comparison with PE_dTH would be better investigated at 235⁰C. However, the relative increase in oxidation stability of PETH F292, was four-fold compared with Herc A. Consequently, by extrapolation, the relative increase of PE_dTH F303 would be significantly higher than that observed for PETH F292. The relative increase in oxidation stability observed with F292 indicates that alkali metal compounds (present inherently) are also synergistic with other aromatic amines.

5. PRELIMINARY OXIDATION-CORROSION TESTS

An oxidation-corrosion test is required in the qualification of a lubricant for subsequent use. The test used is similar to that described in the Military Specification publication (MIL-L-23699A), for a lubricating oil in an aircraft turbine engine.

In the preliminary tests performed, the metals used were silver, aluminum, titanium, and steel (see Appendix A-I-Additives for details). Their cumulative effects on oxidation stability at 220⁰C, of the different basestocks (PETH, PE^dTH, dPE^dTH), were compared with a commercial lubricant Herc A as a reference. The effect of tricresyl phosphate (TCP, 1%), an anti-wear additive, on oxidation stability was also investigated in these tests. However, any corrosion effects on the metals will be investigated in a more detailed study in future work.

The results illustrated in Fig. 4 indicate a relative increase in oxidation stability of both deuterated and non-deuterated PETH esters. In the absence of TCP, the order of increase was PE^dTH >> F292 > Herc A. In the presence of TCP, the order of increase was PE^dTH > dPE^dTH > PETH ~ Herc A + K-stearate (950 ppm K) > Herc A. TCP appears to have an adverse effect on the oxidation stability of PETH and PE^dTH, whereas a small beneficial effect was observed with Herc A. The above results on the addition of an alkali metal compound to Herc A, suggest an efficacy of alkali metal compounds on the oxidation stability in the presence of certain metals. A similar result was observed by Chao (7) and Kjonaas.

In conclusion, the oxidation-corrosion test verifies PE^dTH to be a superior lubricant basestock and warrants further testing for its final qualification (see Recommendation).

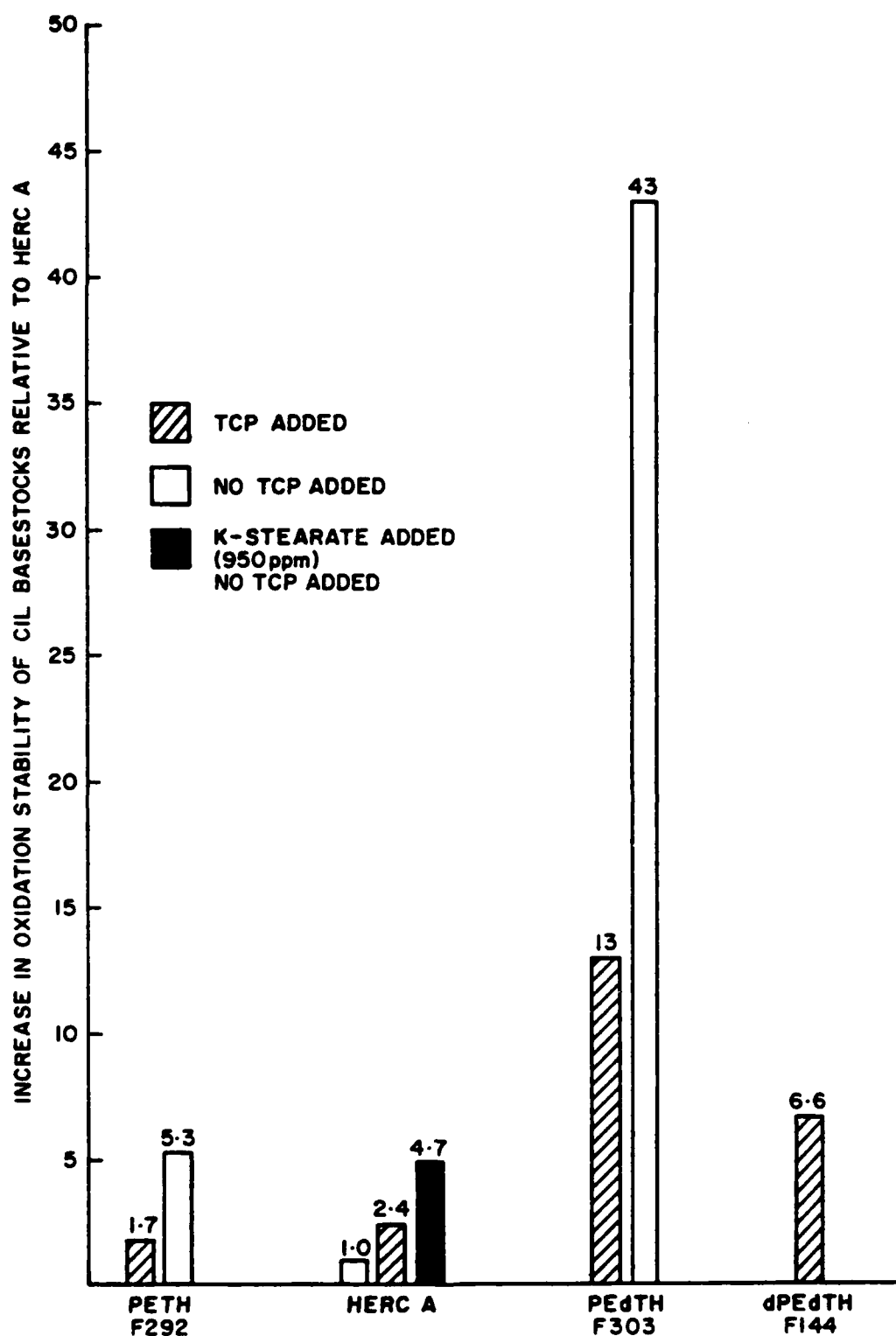


Fig. 4 - OXIDATION-CORROSION TESTS - Comparison of Deuterated and Non-deuterated Basestocks, with Herc A, in presence of: Ag + Al + Ti + Fe, with and without TCP (1%). Anti-oxidant: 0.5% octyl PANA; Oxidation Temp: 220°C

CONCLUSIONS AND RECOMMENDATIONS

The superior lifetime characteristics of a class of deuterated lubricants have been corroborated in a series of oxidation stability tests. The variability in oxidation stability among different batches of similar basestocks appears to be attributable to varying concentration of alkali metal incorporated (fortuitously) in the basestock. The concentration of alkali metal present in the basestock appears critical, a maximum enhancement in oxidation stability is observed followed by a decrease, with increasing alkali metal concentration.

The significant enhancement in oxidation stability exhibited by 97% deuterated esters (PEdTH, dPEdth) appears to be attributable to dual effects of deuteration (approximately threefold, at 220⁰C with 0.5% octyl PANA) and the alkali metal effect (maximum enhancement: approximately thirtyfold under similar oxidation conditions). Consequently, overall lifetime improvements of approximately 100 has been realised with a deuterated ester, compared with a commercial lubricant basestock (Herc A).

While most test results to date have emphasized the extended lifetime characteristics of deuterated lubricants, results can be alternately presented to show elevated temperature performance. For a constant induction period (lifetime) a deuterated lubricant has been shown to operate at a temperature approximately 25⁰C higher than its nondeuterated analog. This result is of great potential interest to engine designers who are currently constrained by the useful operating temperatures of available lubricants. Both the deuteration and alkali metal effect, at this time, have not been thoroughly evaluated as a function of temperature and other environmental factors.

Because of these exciting results, much potential for future work can be identified. Candidate tasks include:

- (1) Determine the physical properties of PEDTH, e.g., viscosity, pour points, etc. This information is necessary prior to the formulation of lubricants for specific applications.
- (2) Conduct oxidation-corrosion tests to further determine the effect of individual metals on PEDTH with and without alkali metal salts, as well as the corrosion aspect of the metal surface.
- (3) Conduct stability tests on a formulated PEDTH whereby other additives, e.g., metal deactivators, etc., are included in addition to anti-oxidant and anti-wear additives.
- (4) Further investigate the synergistic effects of deuteration and alkali metals.
- (5) Quantify the high temperature performance characteristics of deuterated lubricants for potential advanced engine applications.
- (6) Further investigate the alkali metal effect:
 - (a) Mechanistic studies: to elucidate the synergism-mechanism with the anti-oxidant. For example, the role of ionicity: effect of multi-valent ions, as well as the effect of the anion.

- (b) In the presence of other additives.
- (c) Products of degradation as a function of temperature and other additives.
- (d) Applicability to other classes of lubricants.
- (e) Formulation of a basestock for commercial and military applications.

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APPENDIX - EXPERIMENTAL

APPENDIX A - REAGENTS: Additives and Basestocks

Unless specified otherwise, all reagents were used as received from the supplier.

A-I. ADDITIVES

(i) Anti-oxidants:

(a) octyl PANA: N-p-octyl phenyl-alpha-naphthylamine, where the octyl group is 2,2,4,4 tetramethylbutyl. Octyl-PANA is available from Geigy Industrial Chemicals, under the trade name, Irganox LO-6.

(b) PANA: N-phenyl-alpha-naphthylamine is available from Eastman Kodak Co.

(c) DODPA : p,p'-Diocetyl diphenylamine (purified grade) is manufactured by B.F. Goodrich Chemical Co., and distributed by R.T. Vanderbilt Co., Inc., under the trade name Vanlube 81.

(ii) Alkali metal compounds:

(a) The following were available commercially: sodium and potassium carbonate (Fisher Scientific Co.); sodium borohydride, and sodium acetylacetonate (Alfa).

(b) The following were prepared in the usual manner from the appropriate organic acid and an alkali metal carbonate or hydroxide: sodium hexanoate from hexanoic acid (Aldrich, Gold label) and sodium carbonate; sodium perfluoro decanoate from perfluoro decanoic acid (Alfa) and sodium carbonate; sodium and

potassium stearate from stearic acid and the appropriate metal hydroxide.

(iii) Anti-wear: Tricresyl phosphate (TCP) is available from Eastman Kodak Co.; the technical grade used was a mixture of meta (20%) and para (80%) isomers. To remove acidic impurities it was pre-treated by percolation through alumina (chromatographic grade) and Florosil.

(iv) Metal Coupons: The following were employed in selected oxidation-corrosion tests: copper, steel, titanium, aluminum and silver. The quality grade used was as specified by a Military Specification publication (MIL-L-23699B) and the coupons were cut to $\sim 1 \times 0.5 \times 1 \text{ cm}^3$ size, in order to fit the oxidation cells. To achieve a reproducibly clean surface, the metal specimens were cleaned before use in the following manner: the entire surface of each specimen was initially sanded with wet-dry waterproof silicon carbide paper 400-grit, followed with a finer grade (600-grit) of similar type paper. All sandings were done under running water; the specimens (handled hereafter with forceps) were finally washed with acetone, dried and stored under vacuum.

A-II. BASESTOCKS:

(A) General: The basestocks screened belong to the neopentylpolyol ester group of synthetic lubricants. Specifically, these were pentaerythritol tetra esters:

(i) Non-deuterated: pentaerythritol tetrahexanoate (PETH), and Hercolube A (Herc A).

(ii) Deuterated: pentaerythritol perdeutero tetrahexanoate (PEdTH - deuteration of the acid moiety of the ester),

and perdeutero pentaerythritol perdeutero tetrahexanoate (dPEdTH - deuteration of both alcohol and acid moieties of the ester).

NB The relevant non-deuterated, partially deuterated, and totally deuterated pentaerythritol tetrahexanoate esters are referred throughout the text as PETH, PEdTH, and dPEdTH, respectively.

(B) Description

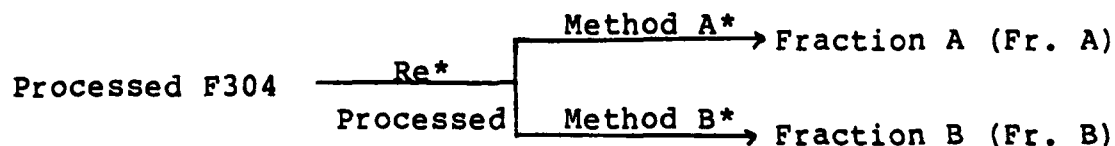
(1) Hercolube A, a commercial lubricant basestock is available from Hercules Powder Co., in Wilmington, DE. It is a mixed ester where the acid moiety is a mixture of C₅-C₉ acids. It was used as a reference with which to compare the other basestocks, since in many respects it is similar in composition and properties to a variety of temperature-stable instrument and aircraft lubricants.

(2) Partially deuterated PEdTH, totally deuterated dPEdTH, as well as the non-deuterated PETH esters were custom synthesized and purchased from 2 commercial laboratories:

(i) KOR Isotopes, Inc., (Cambridge, MA), supplied the original order: 1 batch each of PETH and PEdTH.

(ii) From Cambridge Isotopes Laboratory (CIL), Cambridge, MA, the following were received:

(a) PETH: 4 batches viz F146, F258, F292, F304, plus 2 reprocessed samples ex F304, viz Fraction A, and Fraction B:



* Proprietary information.

(b) PE_dTH: 2 batches viz F145 and F303.

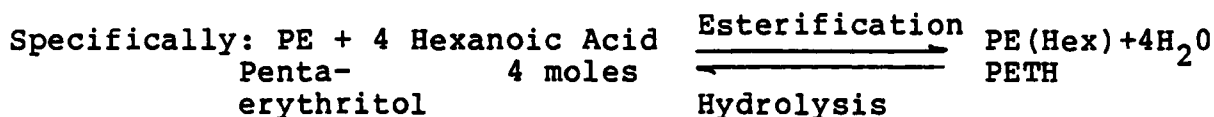
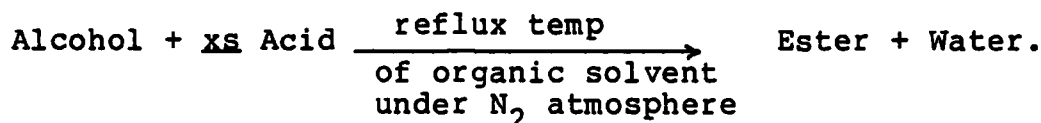
(c) dPE_dTH: F144 (1 batch)

(iii) MCP 386 is a complimentary sample of custom synthesized PETH received from Mobil Oil Corp.

(C) Preparation and Isolation of PETH (Outline)

(This is included because of its relevance to the discussion on the characterization of the ester-basestocks.)

The preparation is summarized in the general equation:



Comments:

(i) A stoichiometric excess of hexanoic acid is used to displace the equilibrium such that esterification goes to completion and hydrolysis does not occur.

(ii) In the presence of a catalyst (p-toluene sulphonic acid), a fairly low boiling solvent (e.g. toluene), is adequate; however, in the absence of a catalyst, a higher boiling solvent is employed (e.g. xylene).

(iii) The extent of the reaction is monitored by measuring the volume of water azeotroped off with the organic solvent, and is collected in a Barrett trap.

Isolation: (Non-deuterated as well as deuterated esters).

From the above equation, it is apparent that the main objective is to remove the unreacted hexanoic acid (since it is used in excess), and the organic solvents. This is carried out using the following work-up procedure:

(i) Neutralization of excess hexanoic acid with an alkali (sodium or potassium) carbonate solution (large volume of excess acid is removed by vac-distillation prior to neutralization).

(ii) Removal of residual alkaline solution via water-wash.

(iii) Removal of trace amounts of water using a desiccant (e.g. sodium sulphate or potassium carbonate).

(iv) Vacuum-distillation to remove the organic solvents.

APPENDIX B - METHOD: Determination of Oxidation Stability

B-I. OXIDATION

Oxidation of the basestocks was carried out in pyrex glass cells (30 cm long, 1 cm inside diameter), containing an inlet tube through which dry filtered air was bubbled; the tip of the inlet tube extended 0.3 cm above the base the cell to facilitate aeration of the small sample volume used (2 ml). The cells were heated in an oven, controlled to $\pm 0.5^{\circ}\text{C}$. Prior to use, the cells were cleaned in a hot nitric/sulfuric acid bath, rinsed repeatedly with distilled water, and dried overnight in an oven.

Unless otherwise specified, the oxidations were performed on the basestock (2 ml), containing N-p-octyl phenyl alpha-naphthylamine (octyl PANA 0.5%), as the anti-oxidant with dry air (flow rate 20 ml/min), and at a fixed temperature (220°C).

B-II. DETECTION AND RECORDING OF OXIDATIVE DEGRADATION

Oxidation stability of a lubricant basestock is determined by measurement of its induction period, which is the time elapsed until oxidative degradation occurs. At the onset of oxidative degradation, a depletion of the anti-oxidant concentration occurs, and this is accompanied by a sharp increase in viscosity, acidity, and peroxide concentration of the basestock. Measurement of these parameters as a function of time, has been the conventional method for determining the induction period of the basestock. This procedure requires periodic sampling for analyses, which are tedious, labour intensive and wasteful of the lubricant sample.

To obviate these problems another technique involving an electronic gas sensor for monitoring the oxidation stability of the basestock was developed by Wohltjen and Ravner (3). These

authors found the evolution of low molecular weight gases and vapors also accompanied oxidative degradation of the lubricant basestock. Consequently, monitoring this gas evolution with a gas sensor provided a simple continuous indication of the lubricant oxidative status.

A block diagram of the experimental apparatus is shown in Fig. (5). Excellent correlation of the sensor method of detection versus the conventional method is illustrated in (Fig. 6).

Initially, a recorder was used to plot the sensor response (voltage output signal) as a function of time. However to obviate the need for many recorders, a computer (Apple II plus) is being used; the data is visualized on a television monitor, and stored on disc; a maximum of 16 oxidation tests can be monitored simultaneously. A further refinement of the system is in the computer programming: conversion of the voltage output signal from the sensor to a parameter involving concentration of the effluent low molecular weight gases and vapors, eliminates the variation in sensitivity among the sensors.

B-III. FORMULATIONS (GENERAL)

Lubricants are generally formulated with a number of additives e.g. antiwear, corrosion inhibitors metal deactivators, viscosity index improvers, etc., in addition to the anti-oxidant(s). However, in the preliminary screening of the basestocks only an anti-oxidant was added, for the objective was to compare their oxidative stabilities relative to a commercial-ester basestock.

B-IV. OXIDATION-CORROSION TESTS

In these tests selected metal coupons are added to a basestock which is formulated with the relevant additives (see B-III). The effect of these metals on the oxidation stability of the basestock can be thus studied as well as any corrosion effects on the metals.

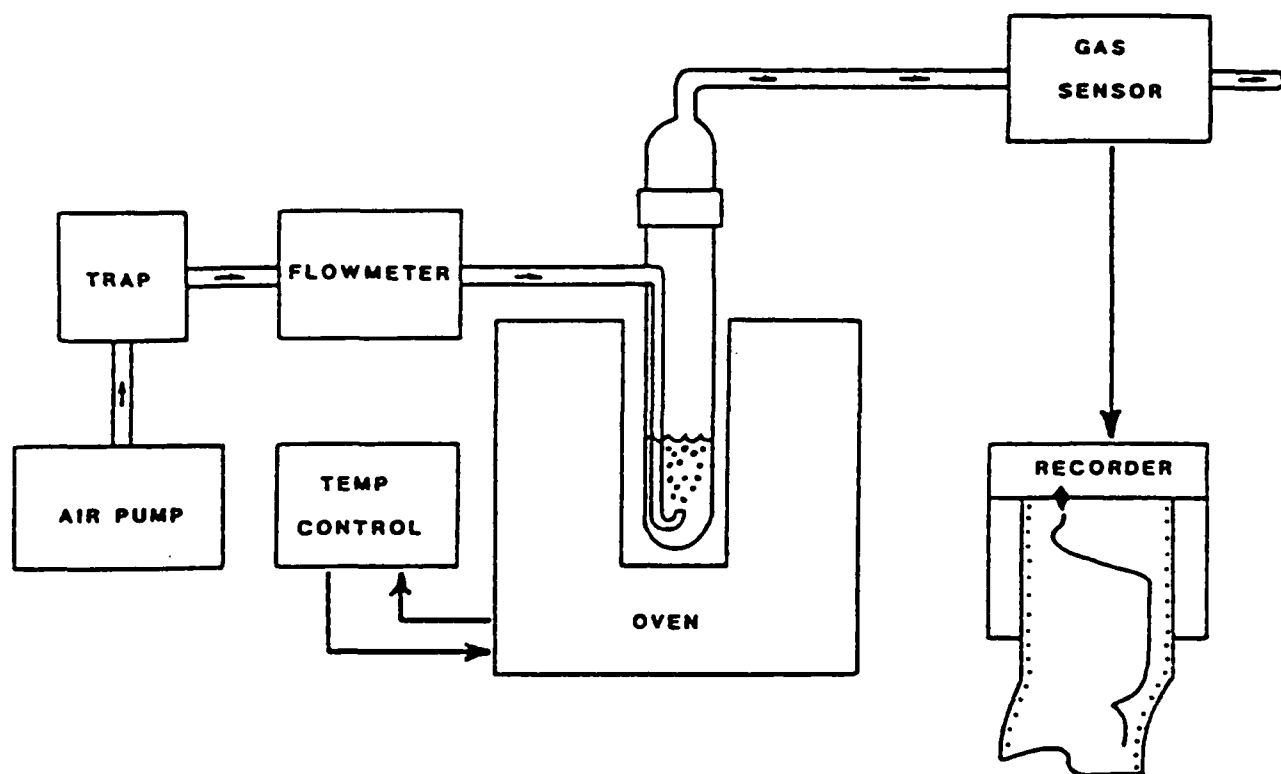


Figure 5. Oxidation test apparatus.

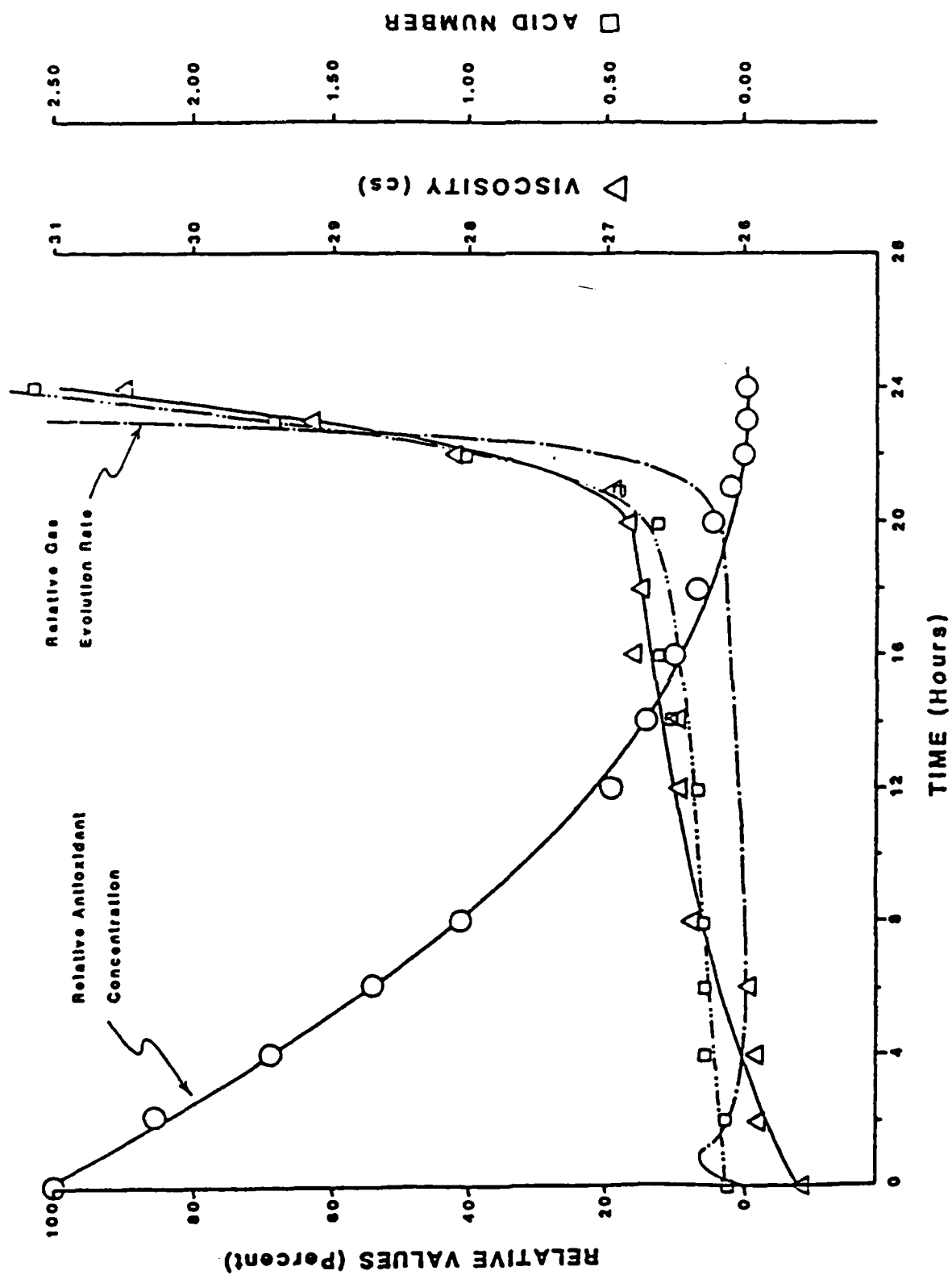


Figure 6. Correlation of oxidative breakdown indicators.

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